63-3-5

REPORT NO.
TDR-169(S3153-01)TN-2

BSD-TDR-63-69

Separation of Some Low Molecular Weight Fluorocarbons by Gas Chromatography

20 MARCH 1963

Prepared by

S. A. Greene and F. M. Wachi

Materials Sciences Laboratory

Prepared for COMMANDER
HEADQUARTERS, BALLISTICS SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
Norton Air Force Base, California

405115

AEROSPACE CORPORATION
LABORATORIES DIVISION •
CONTRACT NO. AF 04(695)-169

BSD-TDR-63-63

Report No.
TDR-169(55153-01)TN-2

SEPARATION OF SOME LOW MOLECULAR WEIGHT FLUOROCARBONS BY GAS CHROMATOGRAPHY

Prepared by

S.A. Greene and F.M. Wachi
Materials Sciences Laboratory

AEROSPACE CORPORATION
San Bernardino Operations

Contract No. AF 04(695)-169

20 March 1963

Prepared for

COMMANDER
HEADQUARTERS, BALLISTICS SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
Norton Air Force Base
California

Report No.
TOR-169(83153-01)TN-2

SEPARATION OF SOME LOW MOLECULAR WEIGHT FLUOROCARBONS BY GAS CHROMATOGRAPHY

Prepared by S.A. Greene and F.M. Wachi
S. A. Greene and F. M. Wachi
Materials Sciences Laboratory

Approved by
Kenneth Pearce
Group Director
Re-Entry Systems Group

Approved by
Darwin C. Middlekauff
Col. USAF
Deputy for Ballistic Missile
Re-Entry Systems

Prepared for

COMMANDER
HEADQUARTERS, BALLISTICS SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
Norton Air Force Base
California

ABSTRACT

A gas-liquid chromatographic separation of some low molecular weight fluorocarbons is described. The separation has been effected at 0°C with a partially fluorinated butylacrylate, $CH_2=CHCO_2CH_2(CF_2CF_2)_3H$ as the liquid phase. As an adjunct to GLC separation, separations were also carried out by GSC on a silica gel column under programmed temperature conditions.

CONTENTS

TABLES

FIGURES

I. INTRODUCTION

A liquid phase has been found which yields excellent results for the gas chromatographic separation of certain low molecular weight fluorocarbons. The efficacy of the material, $CH_2=CHCO_2CH_2(CF_2CF_2)_3H$ is superior to liquid phases previously reported in the literature and is somewhat difficult to rationalize. As an adjunct to gas-liquid chromatography (GLC) separation, separations were also carried out by gas-solid chromatography (GSC) on a silica gel column.

Reed (7) evaluated several liquid phases for the GLC separation of some fluorocarbons (C_5 to C_9). He concluded that fluorocarbon and chlorofluocarbon media give better resolution of fluorocarbon mixtures than hydrocarbon media after evaluating di(2-ethylhexyl) sebacate, $Cl(CF_2CFCl)_3CF_2COOC_2H_5$, Kel-F No. 90 grease, perfluorokerosine, and perfluorotributylamine. Campbell and Gudzinowicz (3) reported the separation of some C_1 to C_4 fluorocarbons on No. 3 Kel-F oil columns of various lengths; one was augmented with a short column containing diisodecylphthalate. Unfortunately, Kel-F oil did not constitute a completely satisfactory liquid phase for fluorocarbon separation.

II. EXPERIMENTAL

APPARATUS AND REAGENTS

The gas chromatographic apparatus consisted of a Beckman GC-2A gas chromatograph to monitor the column effluent and a 20-foot coiled column maintained at 0°. The column was constructed from 1/4 - inch o.d. copper tubing and was packed with packing material consisting of 45- to 60-mesh Chromosorb W and $CH_2=CHCO_2CH_2(CF_2CF_2)_3H$ (courtesy of E.I. du Pont de Nemours & Co., Wilmington, Delaware) in the weight ratio of 70 grams

of Chromosorb W to 30 grams of the liquid substrate. The packing material was prepared in the usual manner by dissolving $CH_2=CHCO_2CH_2(CF_2CF_2)_3H$ in ethyl ether. The carrier gas was helium, and the flow rate measured at room temperature was 95 cc. per minute. For GSC, the apparatus was similar to that described by Greene et al (4). Silica gel (Davison Chemical Co., Division of W. R. Grace Corp., Baltimore, Md.) was ground to 50- to 80-mesh and packed in a 10-foot, 1/4 - inch o.d. copper tube.

Fluorocarbons were obtained from various sources. CF_4, C_3F_8 and a mixture of cis- and trans- C_4F_8-2 were purchased from the Matheson Co., East Rutherford, New Jersey. Cyclo-C_4F_8 (Freon-318) was purchased from E. I. du Pont de Nemours & Company, Wilmington, Delaware. C_2F_6, C_2F_4, n-C_3F_6 and iso-C_4F_8 were obtained by the pyrolysis of cyclo-C_4F_8. Cyclo-C_3F_6 was prepared by the photolysis of C_2F_4 using a low pressure mercury arc (1).

PROCEDURE

The retention volumes of CF_4, C_3F_8 and cyclo-C_4F_8 were obtained in the usual manner from the pure samples. The retention volumes of cis- and trans-C_4F_8-2 were determined after the individual components of the mixture had been identified by infrared spectrometry. The retention volume data for C_2F_6, C_2F_4, and n-C_3F_6 were obtained from the analysis of the pyrolysis products of cyclo-C_4F_8 between the temperature interval of 400° to 1000°. The cyclo-C_4F_8 was pyrolyzed by passing it through a 1/16-inch o.d. stainless steel tube, 16 inches in length, at a flow rate of 1.0 cc. per minute. At 400°, only two peaks were observed which correspond to the equilibrium (5)

$$\text{cyclo-}C_4F_8 \rightleftarrows 2C_2F_4 \quad .$$

At 650°, a single additional peak was generated and was identified as n-C_3F_6 (2). Verification was obtained from the analysis of the pyrolysis products of Teflon, heated at 650° (3, 6), which produced the identical peaks.

At 800°, cis- and trans- C_4F_8-2 and C_3F_8 were identified as was iso-C_4F_8 by the method described by Campbell and Gudzinowicz (3). Between 700°-800°, the yield of C_2F_4 decreased sharply while the adjacent peak, which was assigned to C_2F_6 (2), appeared and increased in size.

DISCUSSION

A gas-liquid chromatogram of a complex, gaseous, fluorocarbon mixture is shown in Figure 1. Relative retention times are summarized in Table 1. The individual components of cis- and trans- C_4F_8-2 mixture were identified by infrared spectrometry. This cis form gave characteristic absorption bands at 5.78, 7.42, 9.0, 10.5, and 13.83μ, while the trans form gave absorption bands at 7.74, 11.27, and 14.6μ. Cyclo-C_3F_6 and n-C_3F_6 were not resolved. The small peak which emerges immediately before n-C_3F_6 was assigned to C_2F_2; it is difficult to conceive of another assignment. The small peak preceding iso-C_4F_8 is probably octafluoro-1-butene (C_4F_8-1).

A gas-solid chromatogram of a similar gas mixture is shown in Figure 2. The temperature was programmed from room temperature to 180° and the separation was completed in 60 minutes. The cis and trans isomers of C_4F_8-2 were not resolved, but n- and cyclo-C_3F_6 could be resolved.

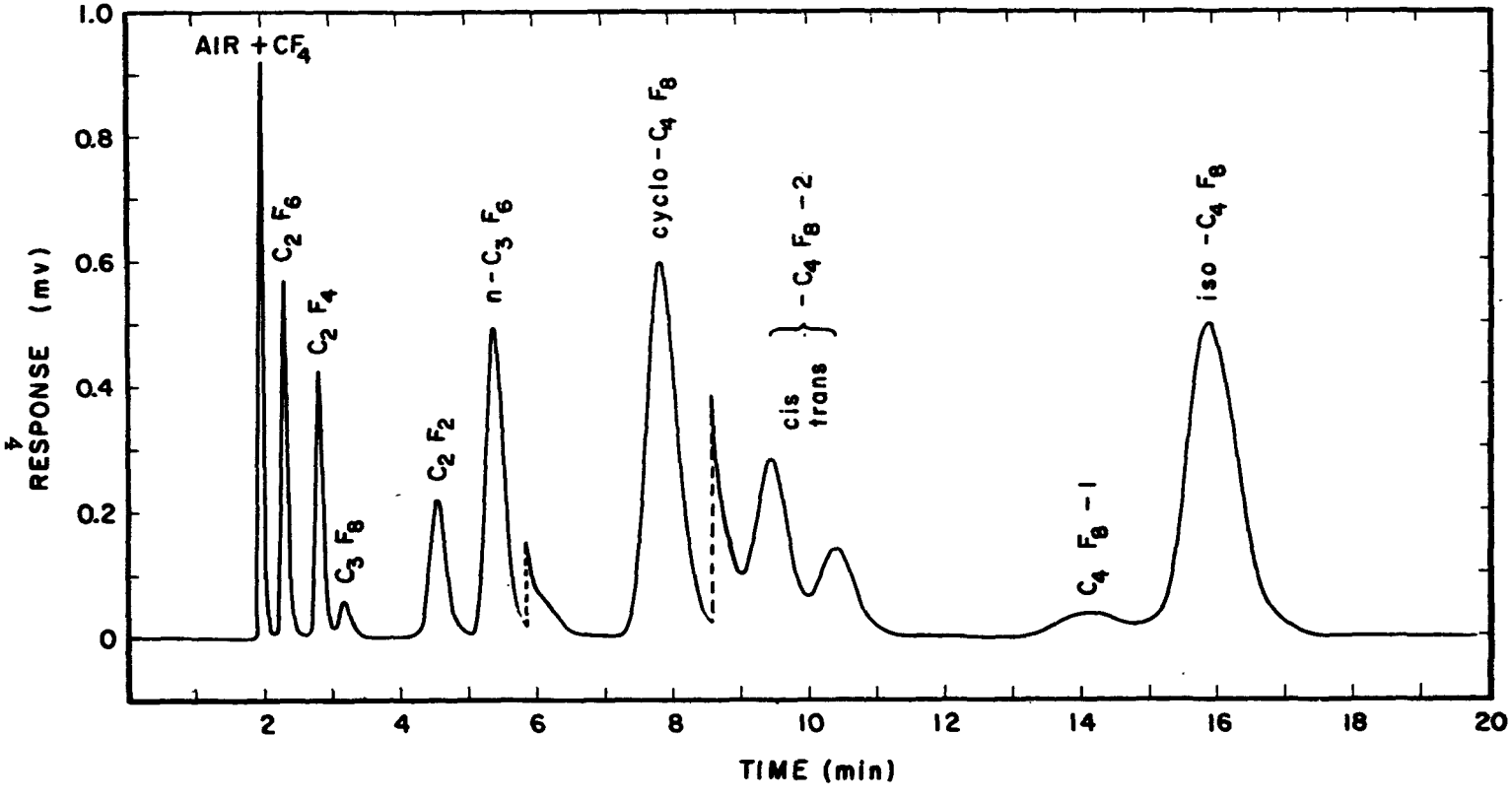

FIGURE 1 GAS-LIQUID CHROMATOGRAM OF PYROLYSIS PRODUCTS OF PERFLUOROCYCLOBUTANE

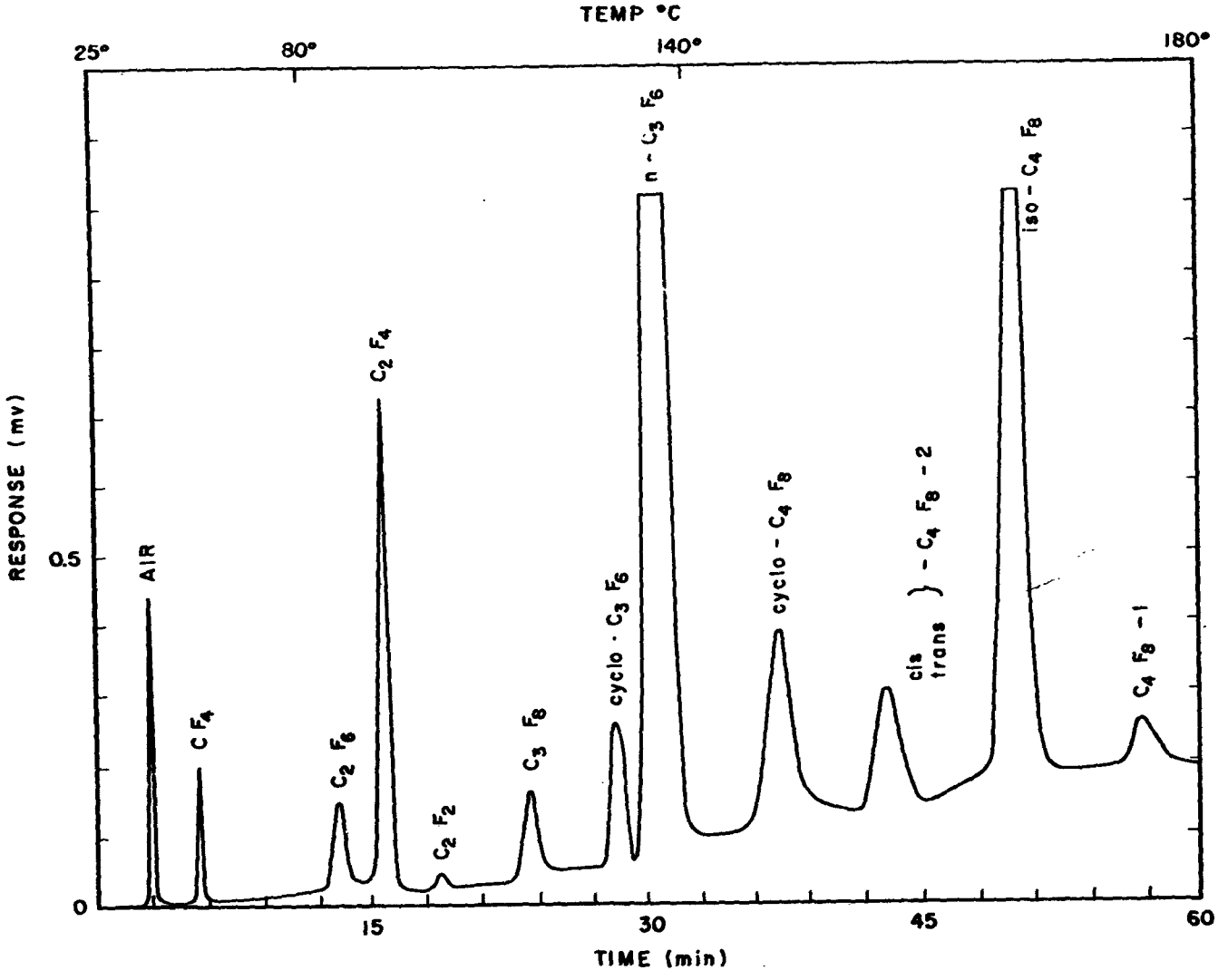

FIGURE 2 GAS-SOLID CHROMATOGRAM OF PYROLYSIS PRODUCTS OF PERFLUOROCYCLOBUTANE

TABLE I

Relative Retention Times

CF_4	0.24
C_2F_6	0.28
C_2F_4	0.35
C_3F_8	0.39
C_2F_2	0.57
n-C_3F_6	0.68
cyclo-C_4F_8	1.00
C_4F_8-2: cis	1.21
C_4F_8-2: trans	1.33
C_4F_8-1	1.82
iso-C_4F_8	2.03

LITERATURE CITED

1. Atkinson, B., J. Chem. Soc., 2684 (1952).

2. Atkinson, B., Atkinson, V.A., J. Chem. Soc., 2086 (1957).

3. Campbell, R.H., Gudzinowicz, B.J., Anal. Chem., 33, 842 (1961).

4. Greene, S.A., Moberg, M.L., Wilson, E.M., Anal. Chem., 28, 1369 (1956).

5. Larcher, J.R., Tompkin, G.W., Park, J.D., J. Am. Chem. Soc., 74, 1693 (1952).

6. Lewis, E.E., Naylor, M.A., J. Am. Chem. Soc., 69, 1968 (1947).

7. Reed III, T.M., Anal. Chem., 30, 221 (1958).

AEROSPACE CORPORATION

TECHNICAL REPORTS – DISTRIBUTION LIST

REPORT TITLE

Separation of Some Low Molecular Fluorocarbons by Gas Chromatography

REPORT NO.	DATE	SECURITY CATEGORY
TDR-169(S3153-01)TN-2	20 March 1963	UNCLASSIFIED

INTERNAL DISTRIBUTION

W. H. Dorrance	SBO
S. A. Greene (20)	SBO
J. E. Colwell	ESO
J. E. Hove	ESO
P. C. Marx	ESO
M. T. O'Shaughnessy	ESO
L. Schieler	ESO
F. M. Wachi (20)	ESO

PREPARED BY S. A. Greene

AEROSPACE FORM 2394

UNCLASSIFIED

Aerospace Corporation, San Bernardino Operations. SEPARATION OF SOME LOW MOLECULAR WEIGHT FLUOROCARBONS BY GAS CHROMATOGRAPHY. Prepared by S. A. Greene and F. M. Wachi, Materials Sciences Laboratory. 20 March 1963. [14] p. incl. illus. (Report TDR-169(S3153-01)TN-2;BSD-TDR-63-63) (Contract AF 04(695)-169) Unclassified report

A gas-liquid chromatographic separation of some low molecular weight fluorocarbons is described. The separation has been effected at 0°C with a partially fluorinated butylacrylate, $CH_2=CHCO_2CH_2(CF_2CF_2)_3H$ as the liquid phase.

As an adjunct to GLC separation, separations were also carried out by GSC on a silica gel column under programmed temperature conditions.

UNCLASSIFIED

UNCLASSIFIED

Aerospace Corporation, San Bernardino Operations. SEPARATION OF SOME LOW MOLECULAR WEIGHT FLUOROCARBONS BY GAS CHROMATOGRAPHY. Prepared by S. A. Greene and F. M. Wachi, Materials Sciences Laboratory. 20 March 1963. [14] p. incl. illus. (Report TDR-169(S3153-01)TN-2;BSD-TDR-63-63) (Contract AF 04(695)-169) Unclassified report

A gas-liquid chromatographic separation of some low molecular weight fluorocarbons is described. The separation has been effected at 0°C with a partially fluorinated butylacrylate, $CH_2=CHCO_2CH_2(CF_2CF_2)_3H$ as the liquid phase.

As an adjunct to GLC separation, separations were also carried out by GSC on a silica gel column under programmed temperature conditions.

UNCLASSIFIED

UNCLASSIFIED

Aerospace Corporation, San Bernardino Operations. SEPARATION OF SOME LOW MOLECULAR WEIGHT FLUOROCARBONS BY GAS CHROMATOGRAPHY. Prepared by S. A. Greene and F. M. Wachi, Materials Sciences Laboratory. 20 March 1963. [14] p. incl. illus. (Report TDR-169(S3153-01)TN-2;BSD-TDR-63-63) (Contract AF 04(695)-169) Unclassified report

A gas-liquid chromatographic separation of some low molecular weight fluorocarbons is described. The separation has been effected at 0°C with a partially fluorinated butylacrylate, $CH_2=CHCO_2CH_2(CF_2CF_2)_3H$ as the liquid phase.

As an adjunct to GLC separation, separations were also carried out by GSC on a silica gel column under programmed temperature conditions.

UNCLASSIFIED

UNCLASSIFIED

Aerospace Corporation, San Bernardino Operations. SEPARATION OF SOME LOW MOLECULAR WEIGHT FLUOROCARBONS BY GAS CHROMATOGRAPHY. Prepared by S. A. Greene and F. M. Wachi, Materials Sciences Laboratory. 20 March 1963. [14] p. incl. illus. (Report TDR-169(S3153-01)TN-2;BSD-TDR-63-63) (Contract AF 04(695)-169) Unclassified report

A gas-liquid chromatographic separation of some low molecular weight fluorocarbons is described. The separation has been effected at 0°C with a partially fluorinated butylacrylate, $CH_2=CHCO_2CH_2(CF_2CF_2)_3H$ as the liquid phase.

As an adjunct to GLC separation, separations were also carried out by GSC on a silica gel column under programmed temperature conditions.

UNCLASSIFIED